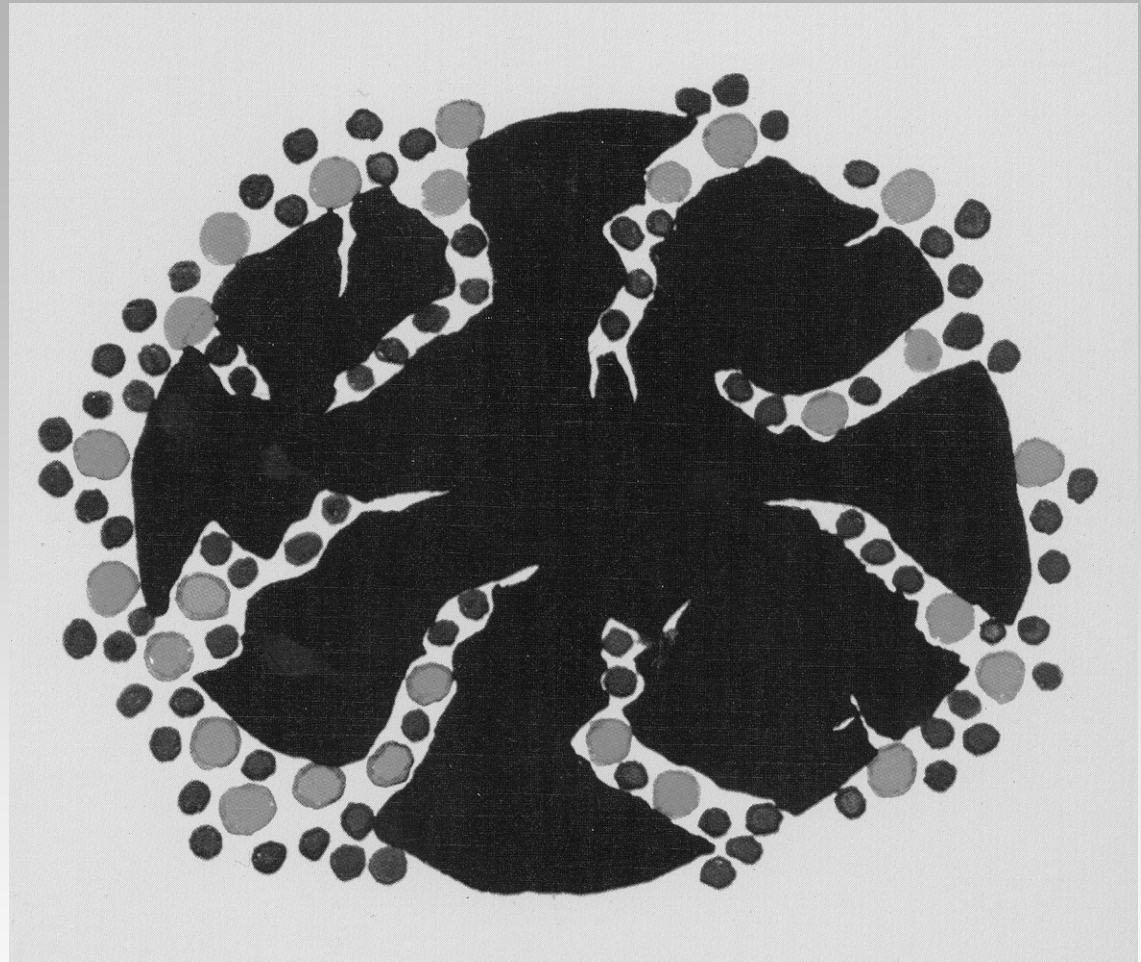


# Fundamentals of Adsorption for Arsenic Removal from Water

Dennis Clifford  
University of Houston

Adsorption is  
taking stuff  
(arsenic) out of  
water and  
putting it onto  
a solid  
adsorbent with  
micro and  
macro pores.



*Application of Adsorption to  
Wastewater Treatment  
W. W. Eckekfelder, Jr., Ed., 1981*

## More Specifically

- **Adsorption** is contaminant removal from water by attachment onto the surface of a porous solid adsorbent (GAC, AAI, GFH/GFO).
  - Physical Adsorption, low energy, reversible
  - Chemical Adsorption, high energy, irreversible
- **Absorption** is contaminant removal by dissolution/reaction in another phase  
Removal of CO<sub>2</sub> by bubbling through NaOH soln.  
$$\text{CO}_2 (\text{g}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaHCO}_3(\text{aq})$$
- ***Sorption*** covers all mechanisms and is the removal of a “sorbate” (contaminant) by a “sorbent” (adsorbent).

# Here is the difference between Adsorption and Absorption



**ADsorption**



**ABsorption**

# “Sorption”: A General Term Covering Many Processes

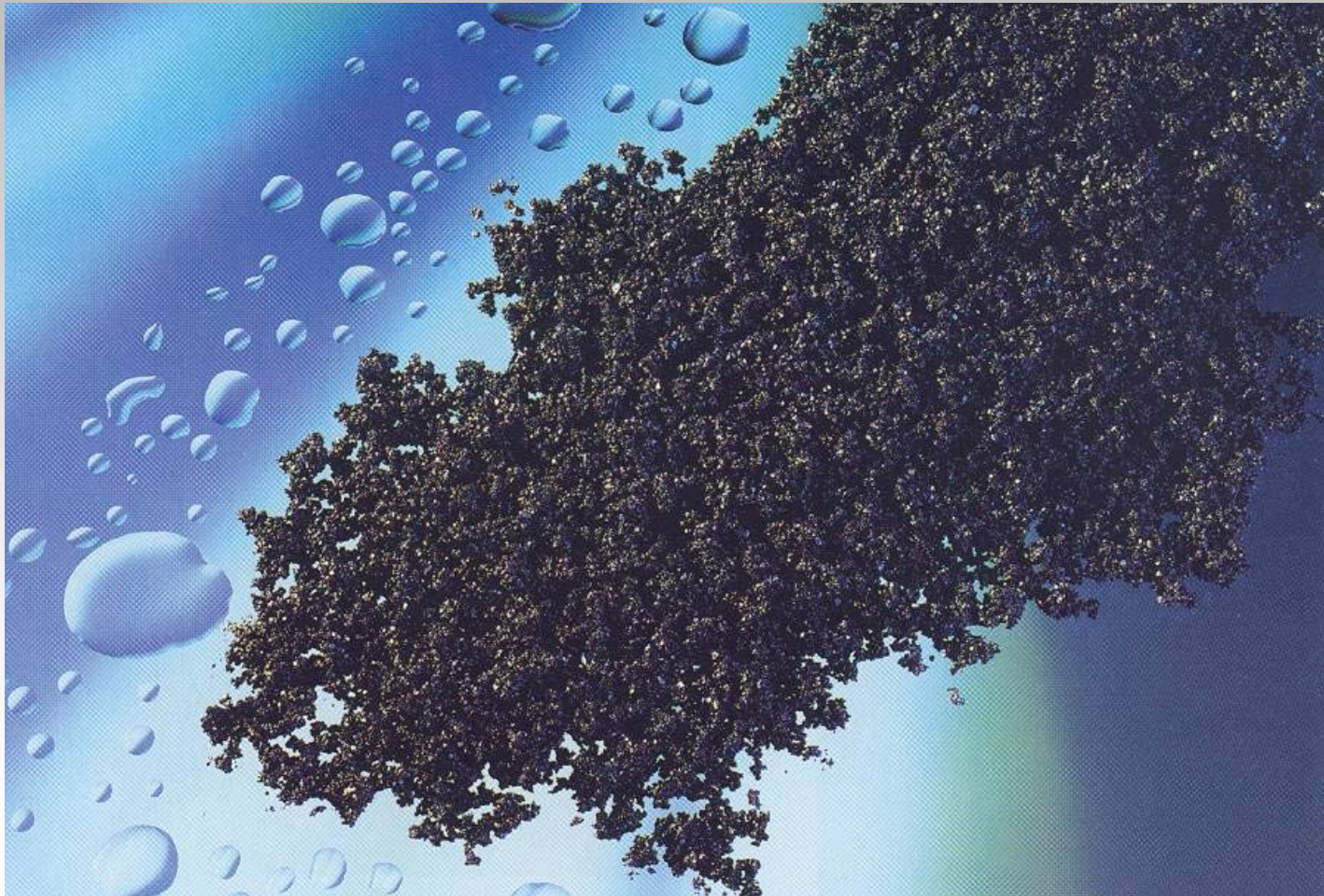
- Physical Adsorption;  $<20$  kJ/mol
  - $\text{GAC} + \text{N}_2 = \text{GAC} \cdot \text{N}_2$ , Reversible
- Chemical Adsorption; up to 800 kJ/mol
  - $\equiv\text{C} + \text{O}_2 \rightarrow \equiv\text{CO}$ ; Irreversible
- Surface Complexation (Ligand Exchange)
  - $\text{FeOOH} + \text{HAsO}_4^- \rightarrow \text{FeO} \cdot \text{HAsO}_4 + \text{OH}^-$
- Ion Exchange (Softening with IX Resin)
  - $2\text{RNa} + \text{Ca}^{2+} = \text{R}_2\text{Ca} + 2 \text{Na}^+$ ;  $< 8\text{kJ/mol}$
- Surface Precipitation

## Common *Sorbents* (Porous Solids) for Water and Wastewater Treatment

- Activated Carbon (GAC 16x40, PAC <325)
- Polymeric Adsorbents (XAD Resins, 16x50)
- Activated Alumina ( $\text{AlOOH}$ , 28x48)
- Granular Ferric Hydroxide/Oxide, GFH/O)
- Zeolites (Aluminosilicate ion exchangers)
- Ion Exchange Resins (Cation and Anion, 16x50)



# Granular Ferric Hydroxide



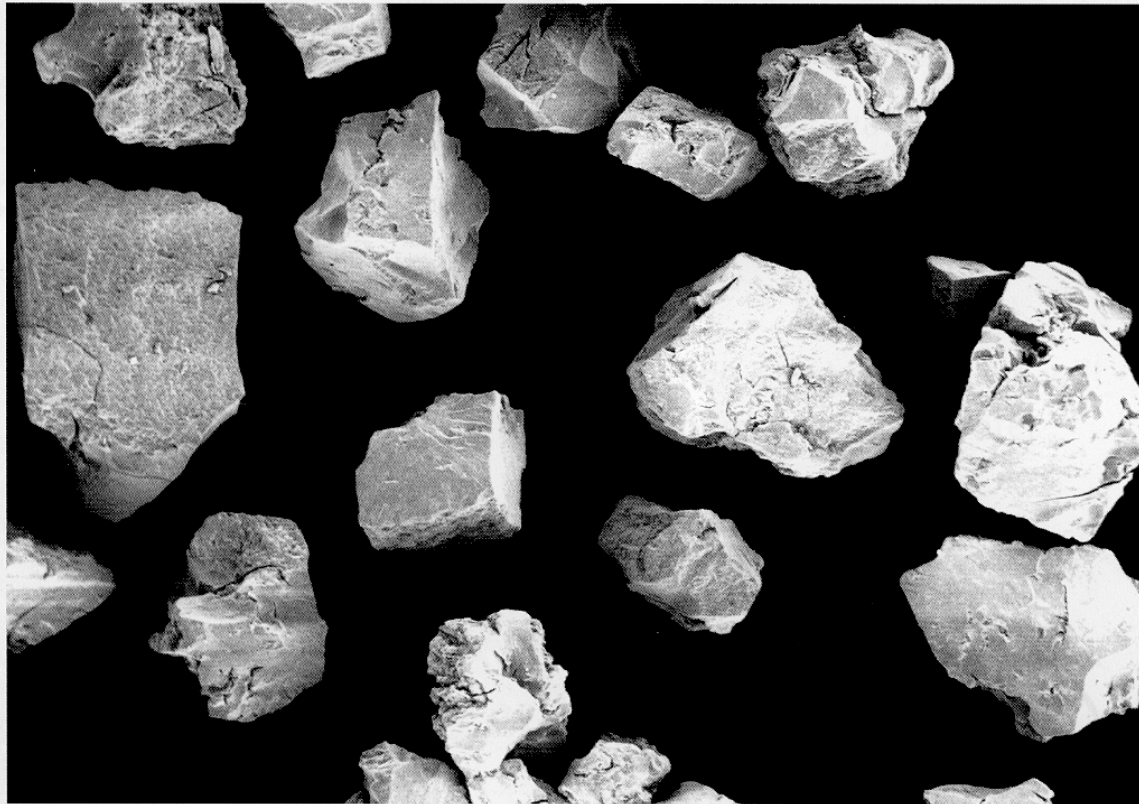


# Granular Ferric Oxide, GFO



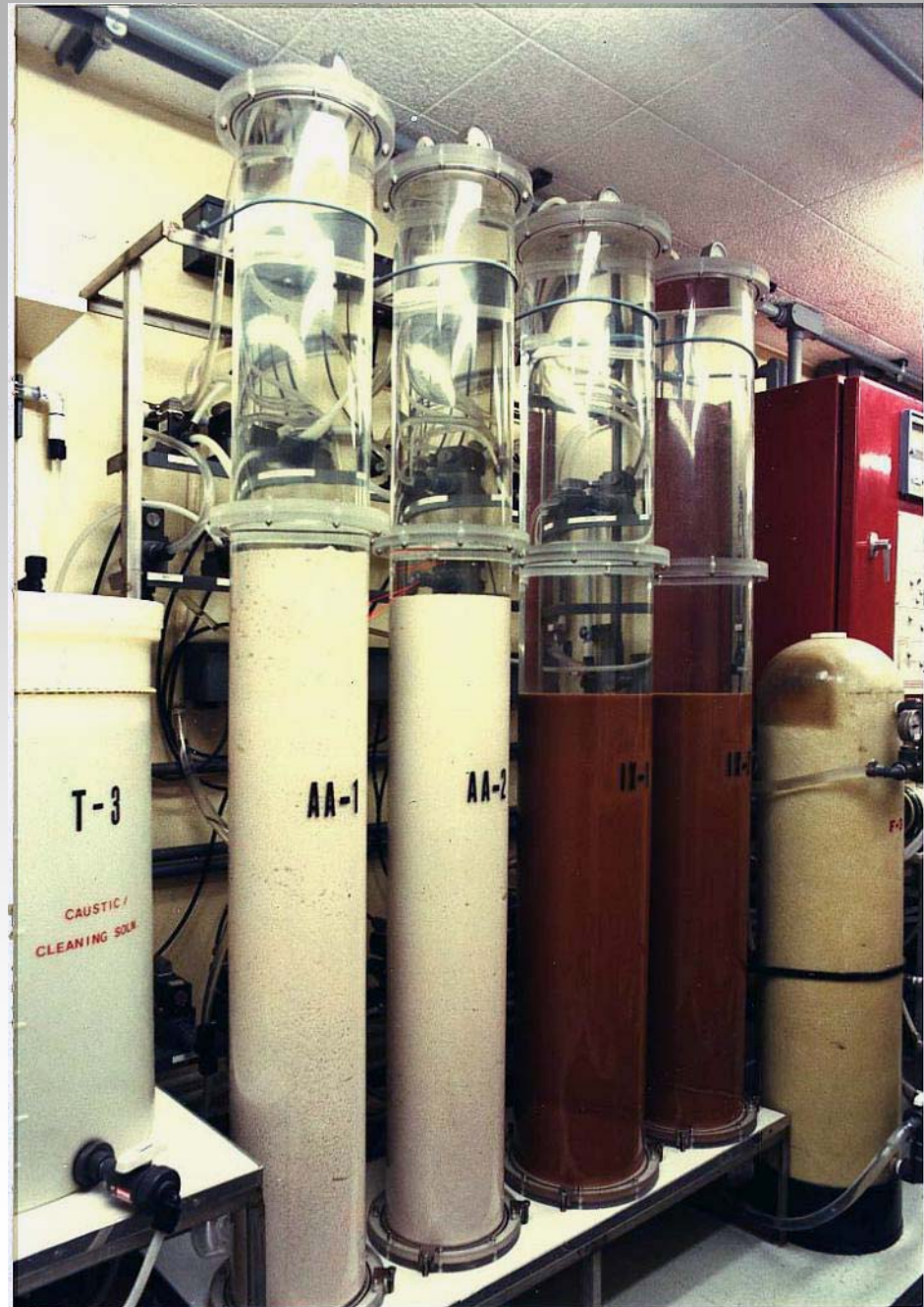


# GFH Magnified



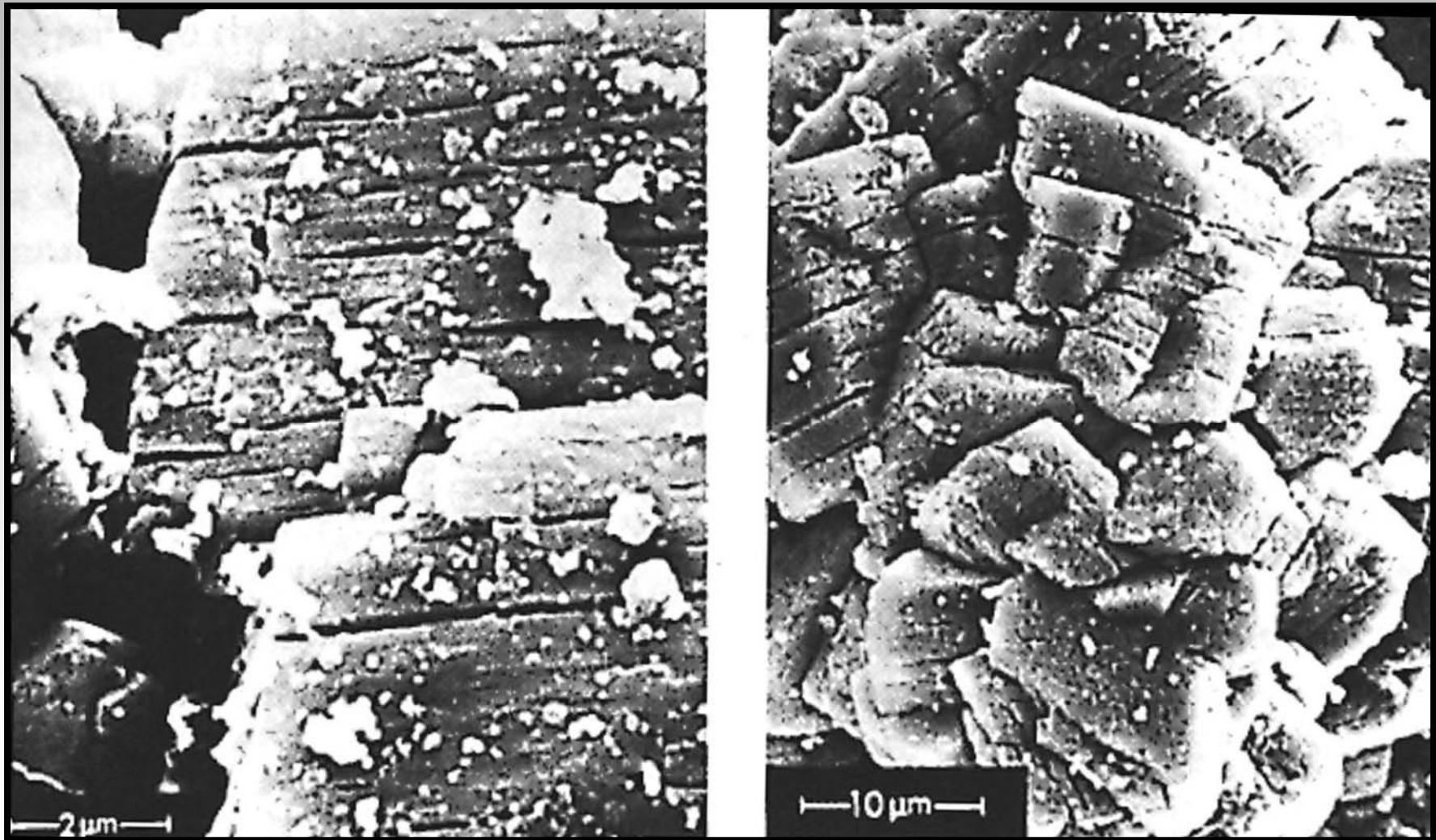
*GEH® is a pure synthetic ferric hydroxide with approx. 75 % porosity and a specific surface area of 250 300 m<sup>2</sup>/g.*

# Activated Alumina in Columns





# Highly Magnified Activated Alumina

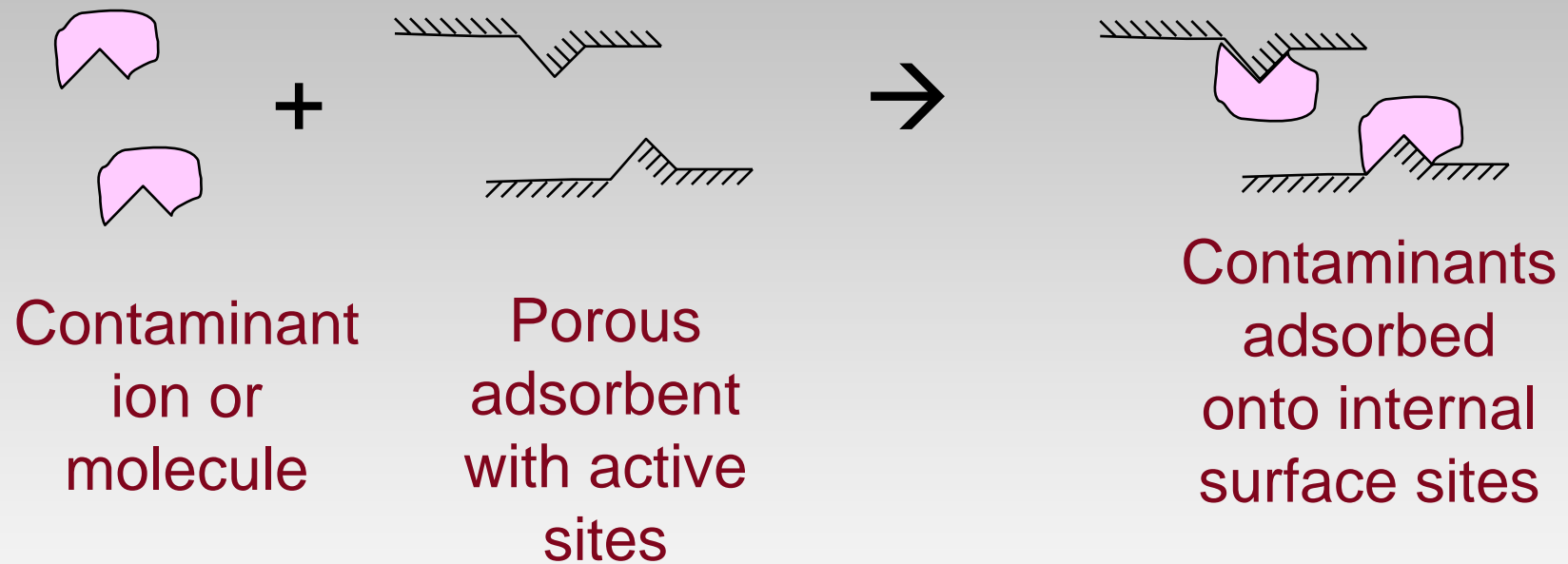


# Characterization of Sorbents, AAl

- Surface area: 200-300 m<sup>2</sup>/g
- Pore volume, 0.2-0.5 cm<sup>3</sup>/g
- Pore size distribution, micro and macro pores.
- Bulk density, 50 lbs/ft<sup>3</sup>
- Skeletal density, 3 g/cm<sup>3</sup>
- Particle size: 28 x 48 mesh (0.6-0.3 mm)
- pH at Zero Charge Point, pH<sub>ZPC</sub>



# Modeling The Adsorption Process



The “Adsorption Isotherm” describes the extent of adsorption at equilibrium.

- **Isotherm:** Constant temperature plot of solid-phase concentration (A•S) vs liquid-phase concentration of contaminant (A).
- **Example:** Simple linear isotherm

$$C_{A,\text{Solid}} = KC_{A,\text{liquid}}$$

$$q_{A,\text{equil.}} = KC_{A,\text{equil.}}$$

$$q_e = KC_e$$

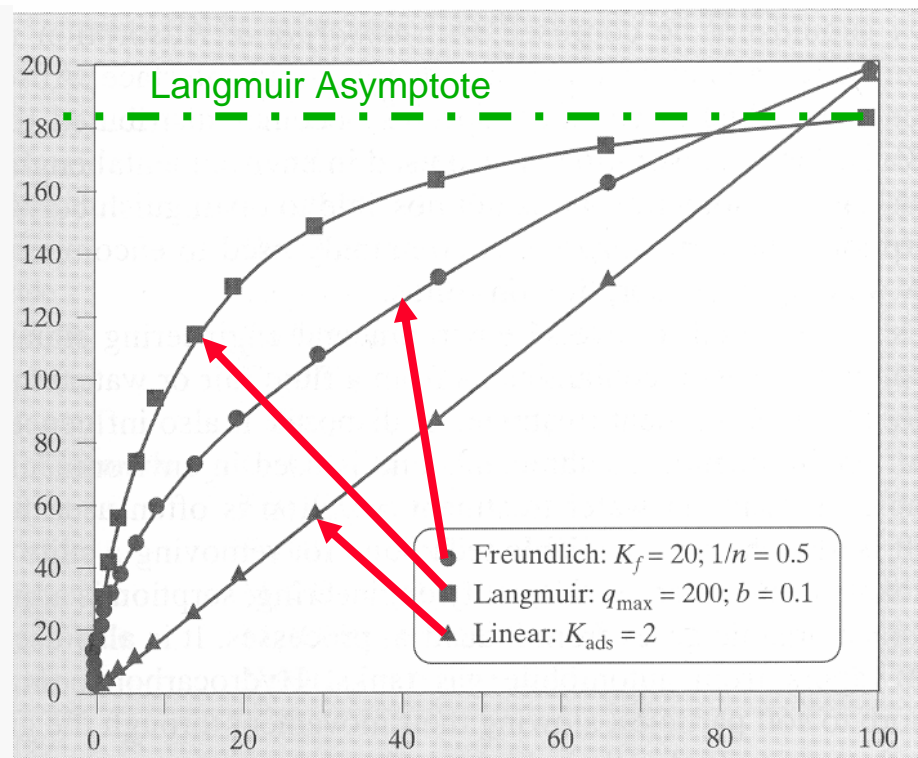
# Common Isotherm Equations

Linear:  $q_e = K_{\text{ads}} C_e$

Langmuir:  $q_e = q_{\text{max}} \frac{bC_e}{1 + bC_e}$

Freundlich:  $q_e = K_f C_e^{1/n}$

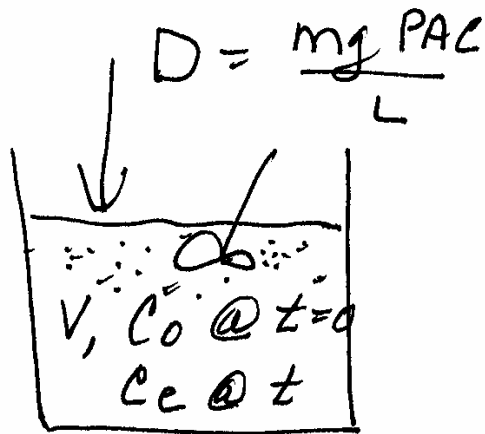
$q_e$ , Solid-phase  
concentration,  
mg A/g AAI,  
y-axis



$C_e$ , Aqueous-phase concentration,  
mg A/L, x-axis

# Construction of an Isotherm from Batch Equilibrium Data

## Nomenclature



$V$  = volume of liquid, L

$C_0$  = initial conc. of contaminant, mg A/L

$M$  = mass of adsorbent added to reactor, mg PAC

$D$  = dosage of adsorbent, mg PAC/L

$D = \frac{M}{V} = \text{mg PAC/L of water}$

## Test Procedure

- (1) Grind adsorbent into powder
- (2) Place volume,  $V$ , of water into reactor (or bottle).
- (3) Add mass ( $M$ ) to volume ( $V$ ) of water.  
 $D = \frac{M}{V} = \text{mg PAC/L of water}.$
- (4) Mix, shake, or tumble mixture for 30 min to 7 days.
- (5) Settle, centrifuge, or filter out the spent PAC.
- (6) Measure  $C_e$ , mg A/L, at equilibrium.
- (7) Repeat steps 2-6 for other dosages of PAC.
- (8) Using data from each batch equilibration, construct an isotherm.

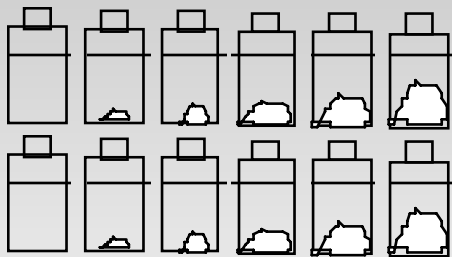


# Equilibrium Isotherm Tests:

## “Bottle-Point” Method for Resins and Adsorbents

---

16x50 mesh resin or  
60x100 mesh alumina  
100-mL Sample



Analyze  $C_0$

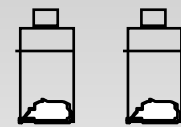


Tumbler

(10 rpm)  
24-48 hrs.



Equilibrium



Analyze  
filtrate,  $C_e$ .



Sample  
by syringe  
Filter ( $0.2\ \mu\text{m}$ )



Measure pH

## Adsorption of arsenic onto aluminum and iron oxides involves:

- Surface complexation (ligand exchange or inner-sphere complex formation)
- Ion Exchange (weak ionic attraction in the diffuse layer)
- Surface precipitation

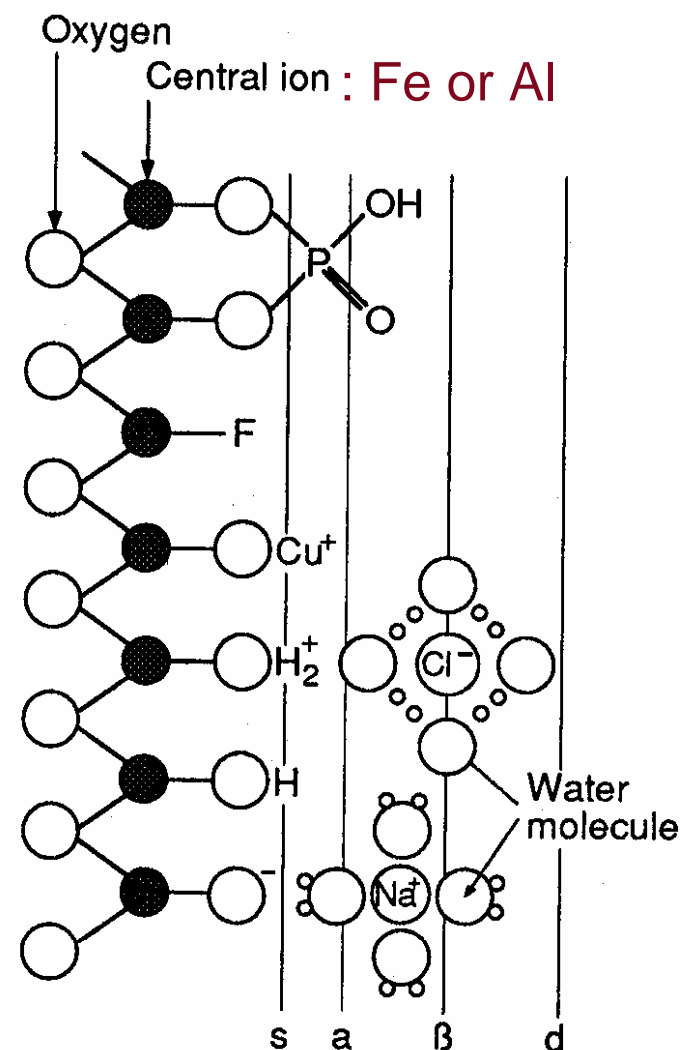
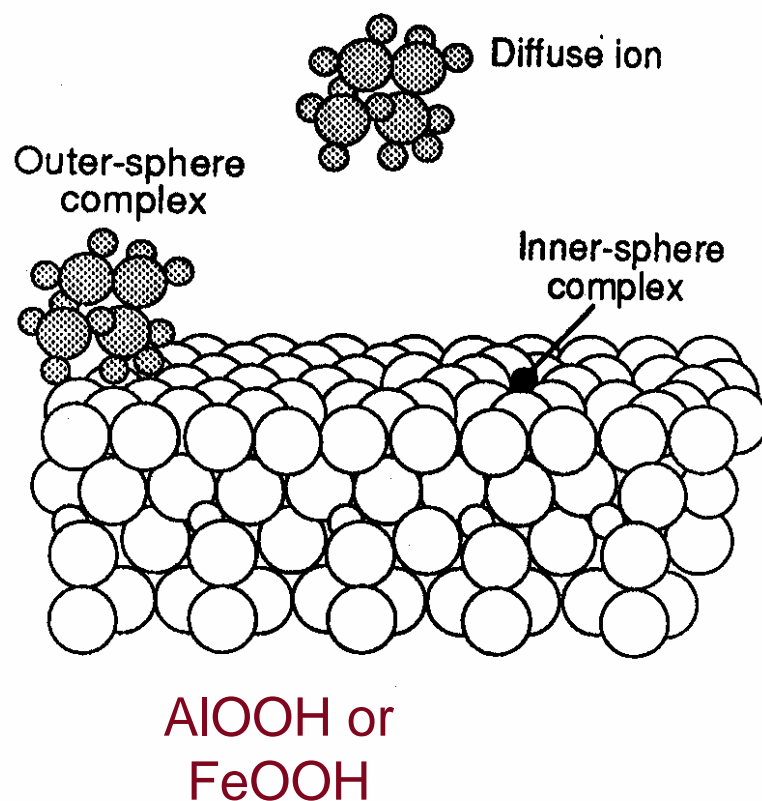
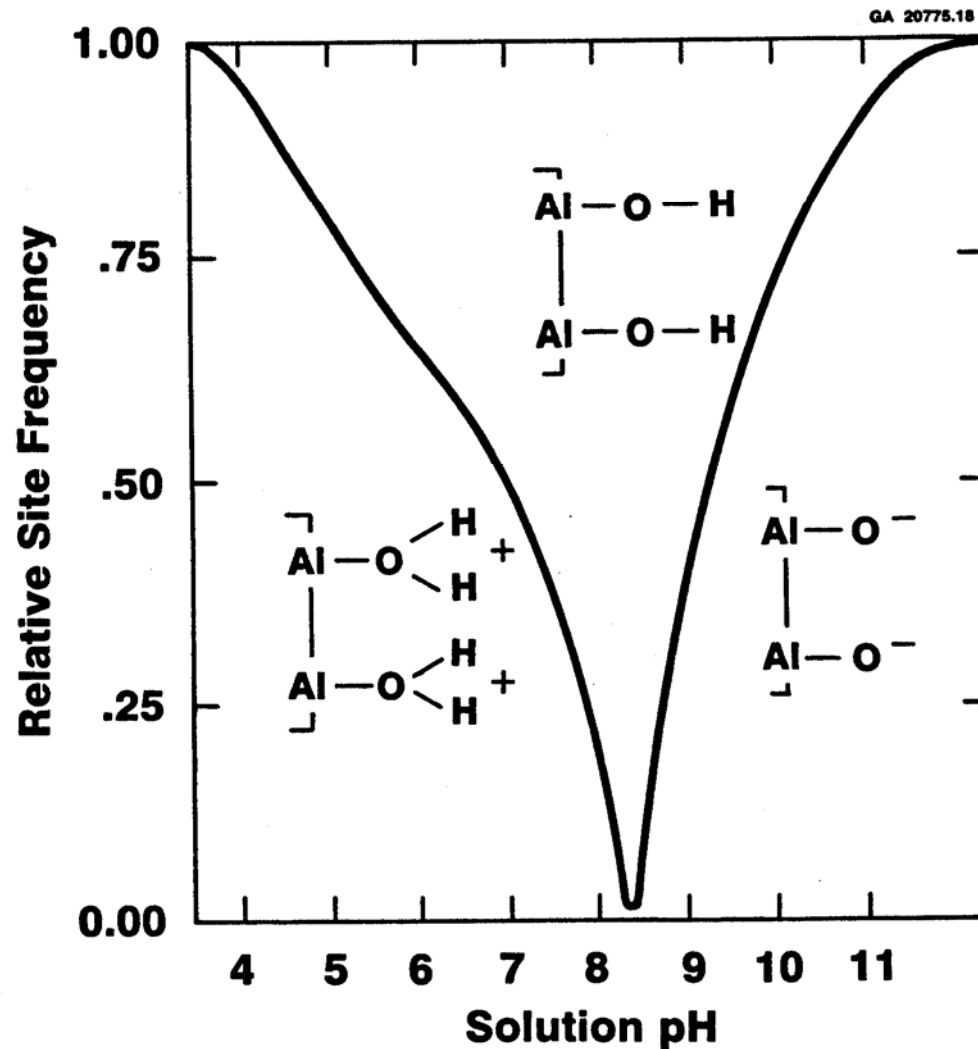


Figure 2.4

Surface complex formation of an ion (e.g., cation) on the hydrous oxide surface. The ion may form an inner-sphere complex ("chemical bond"), an outer-sphere complex (ion pair) or be in the diffuse swarm of the electric double layer. (From Sposito, 1989)

Fig. b shows a schematic portrayal of the hydrous oxide surface, showing planes associated with surface hydroxyl groups ("s"), inner-sphere complexes ("a"), outer-sphere complexes ("β") and the diffuse ion swarm ("d"). (Modified from Sposito, 1984)

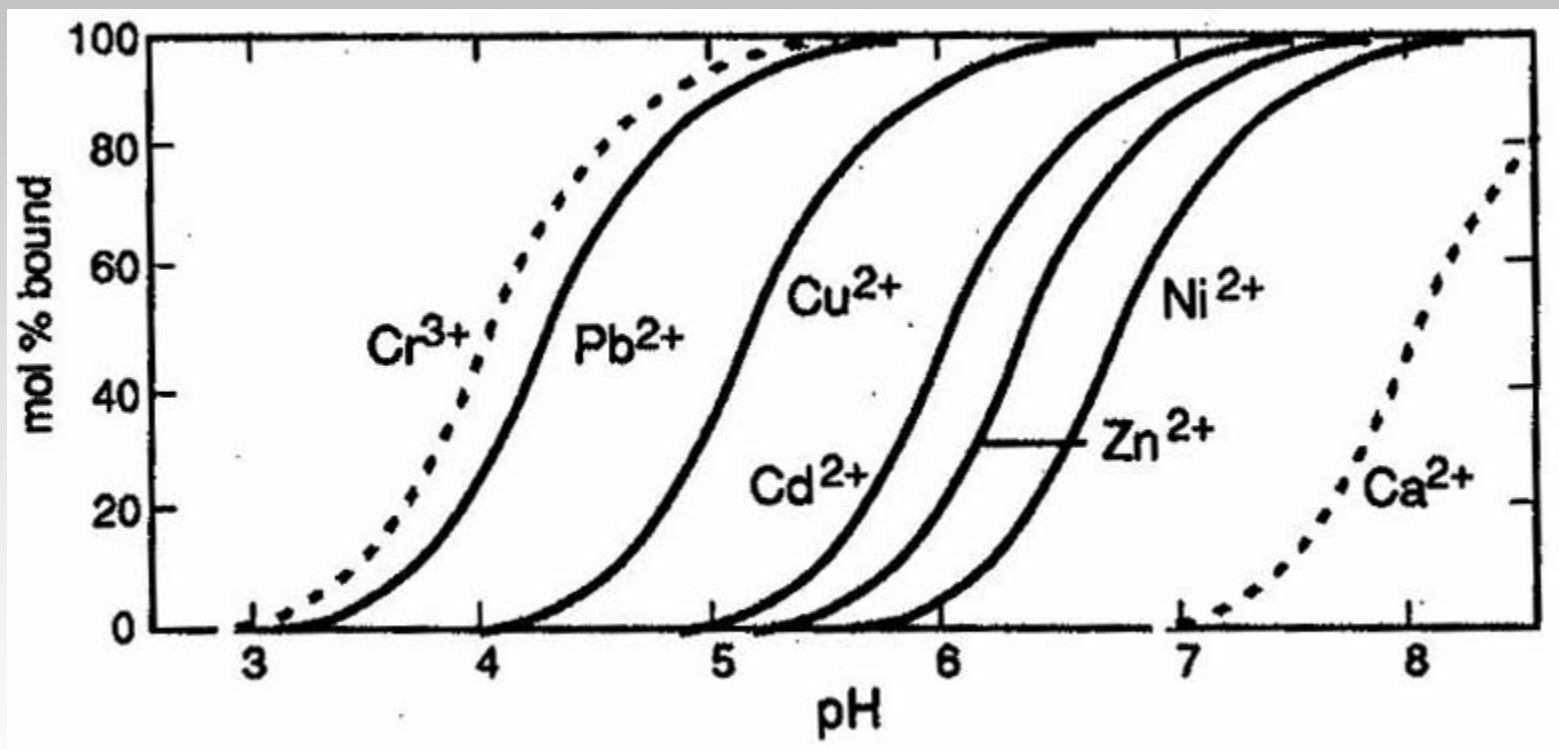


## Relative Site Distribution of an Alumina Surface

. W. Novak, Jr. and R. R. Burr, "Investigations of ion adsorption interactions using flow calorimetry", Alcoa Report 6-887-31

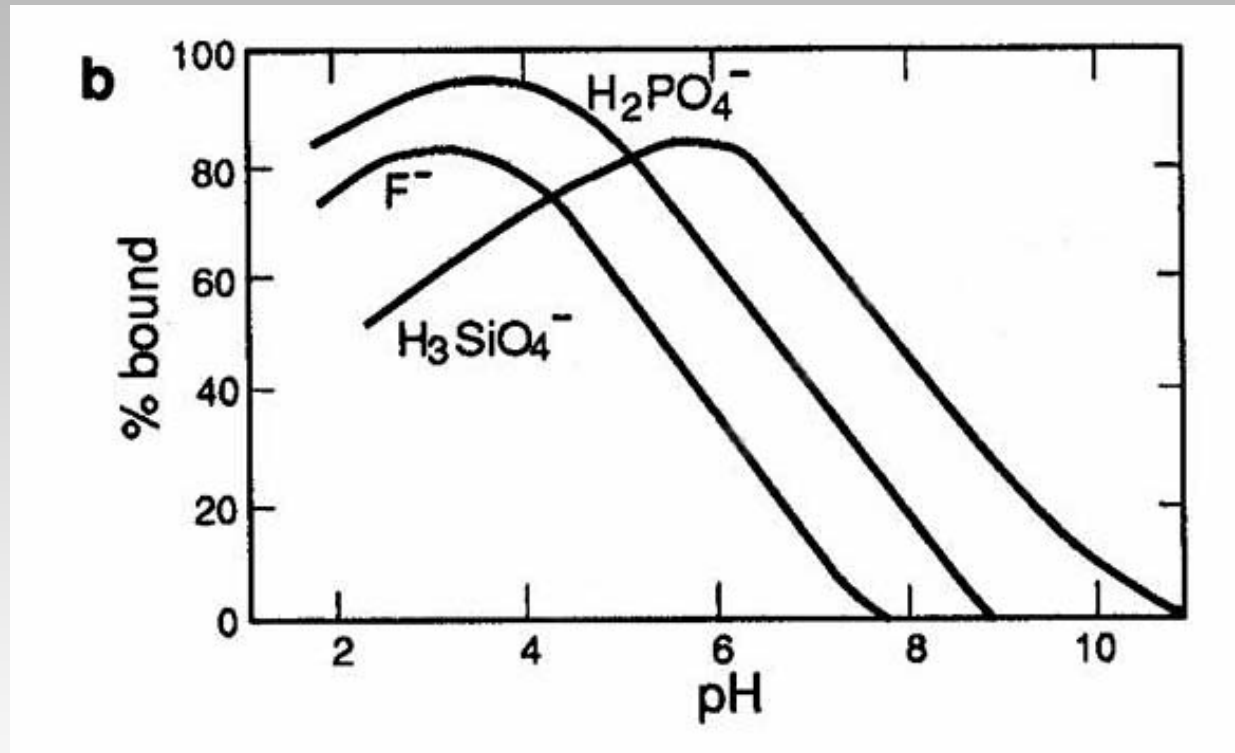


# Cation Sorption onto FeOOH by Outer-Sphere Surface Complex Formation



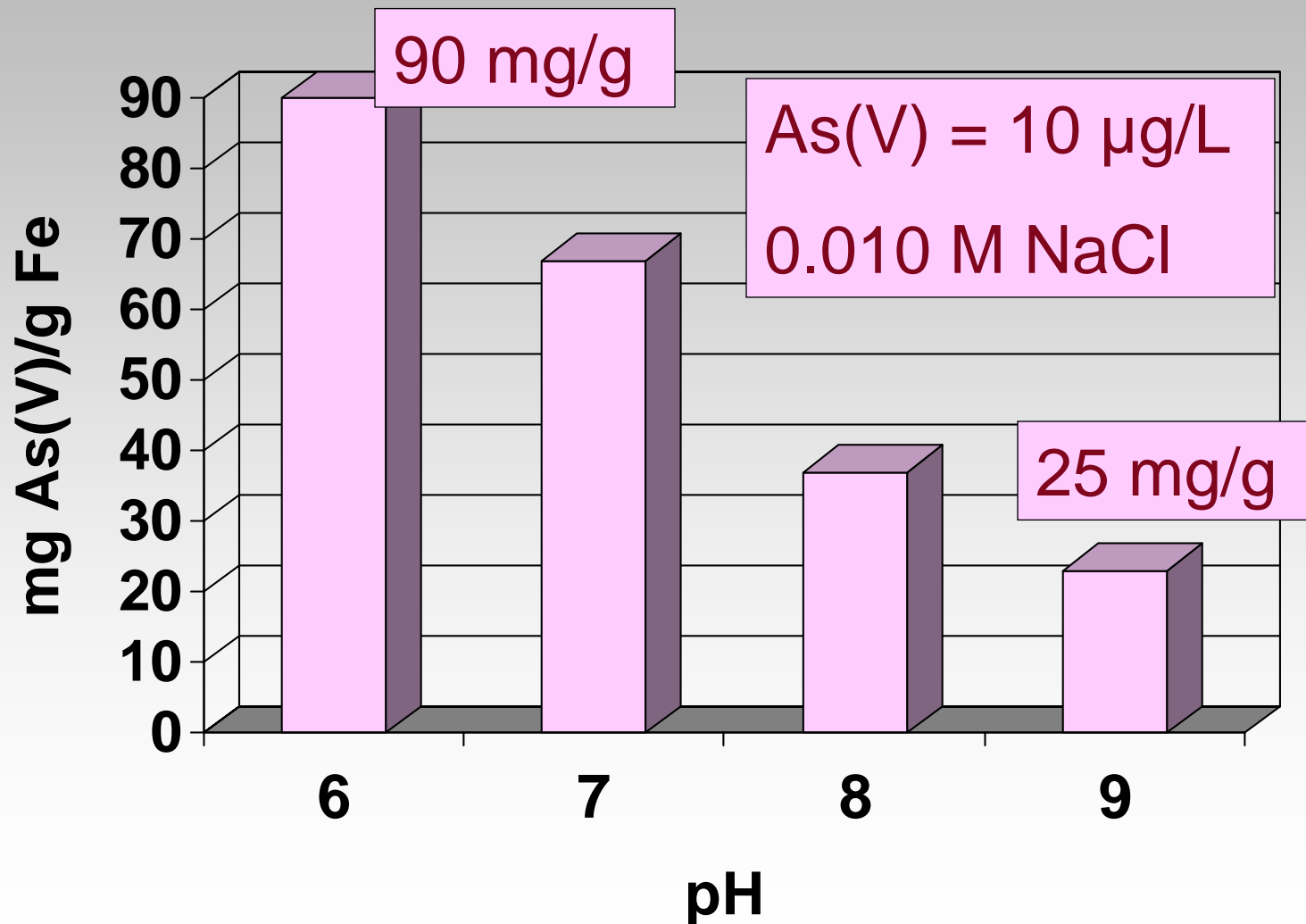
[TOT-Fe] =  $10^{-3}$  M,  $2 \times 10^{-4}$  M reactive sites/L, [TOT-Me] =  $5 \times 10^{-7}$  M, I = 0.1 M NaNO<sub>3</sub>

# Anion Adsorption onto FeOOH

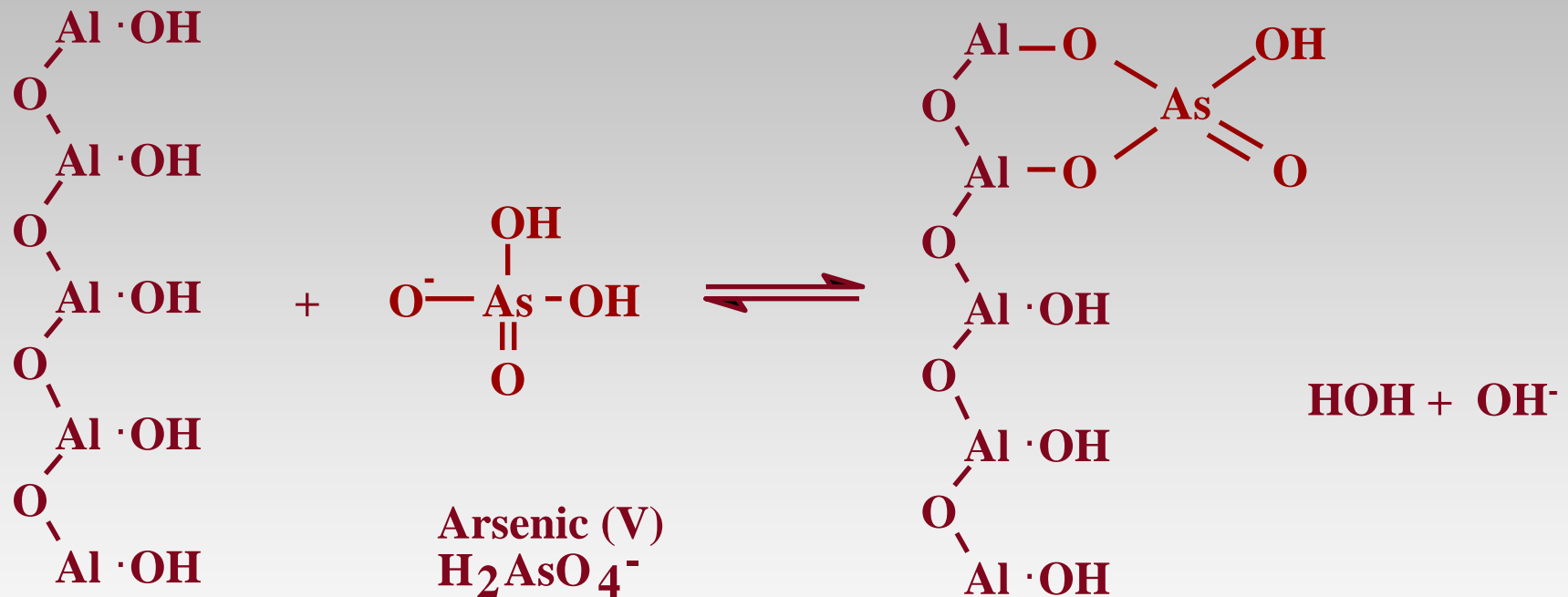


Binding of phosphate, silicate, and fluoride on goethite ( $\alpha$ -FeOOH); the species shown are surface species. (6.0 g FeOOH/L,  $P_T = 10^{-3}$  M,  $\text{Si}_T = 8 \times 10^{-4}$  M.) Sigg and Stumm, 1981

# Effect of pH on GFH Performance



# AAI—Arsenic Ligand Exchange



Alumina  
AlOOH  
FeOOH  
Zr, Ti oxides

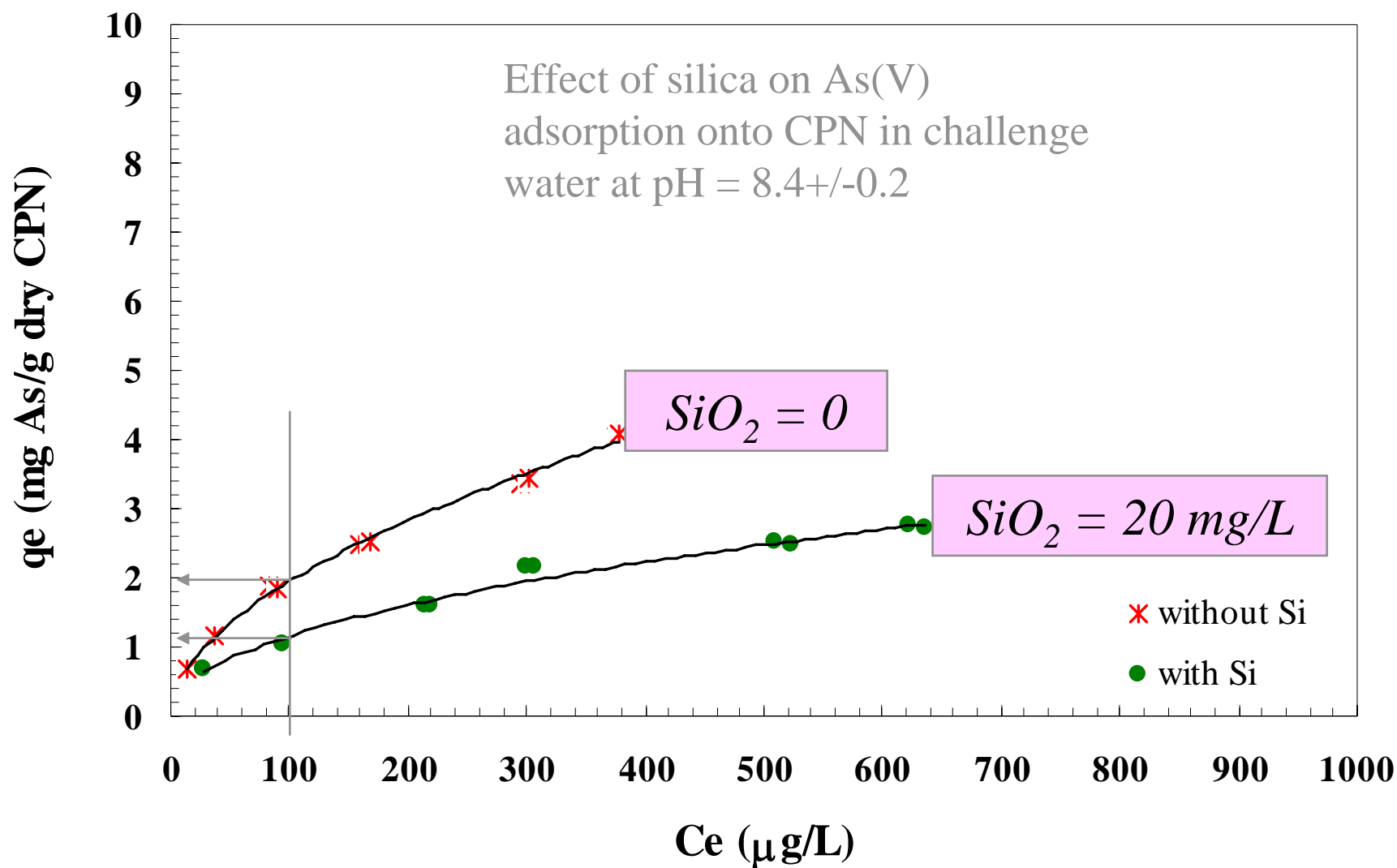
Competing Ligands:  
 $\text{H}_2\text{PO}_4^-$   
 $\text{Si}(\text{OH})_3\text{O}^-$

Arsenic on  
AlOOH  
FeOOH

Hydroxide



# Isotherms for adsorption of As(V) onto CPN AAl



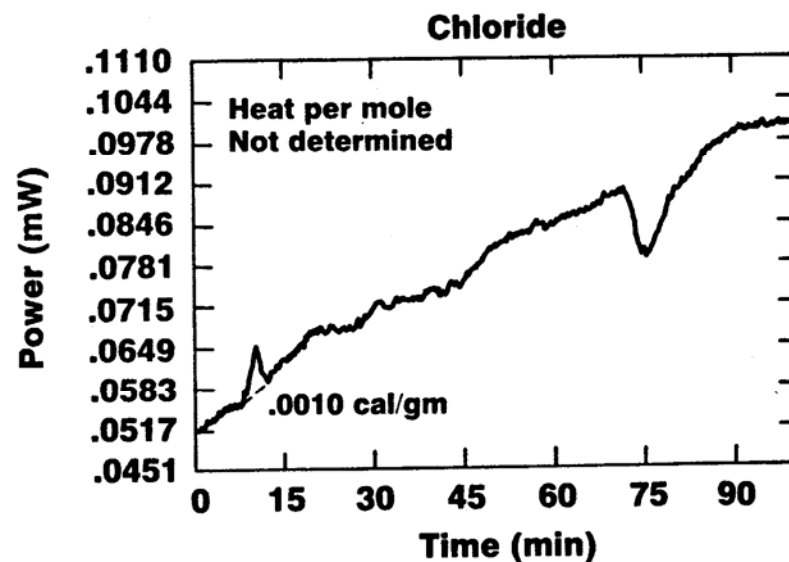
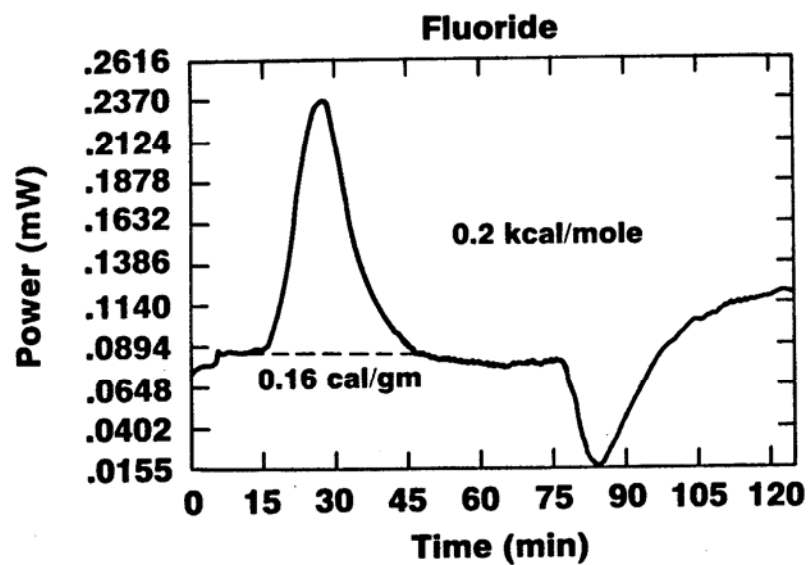
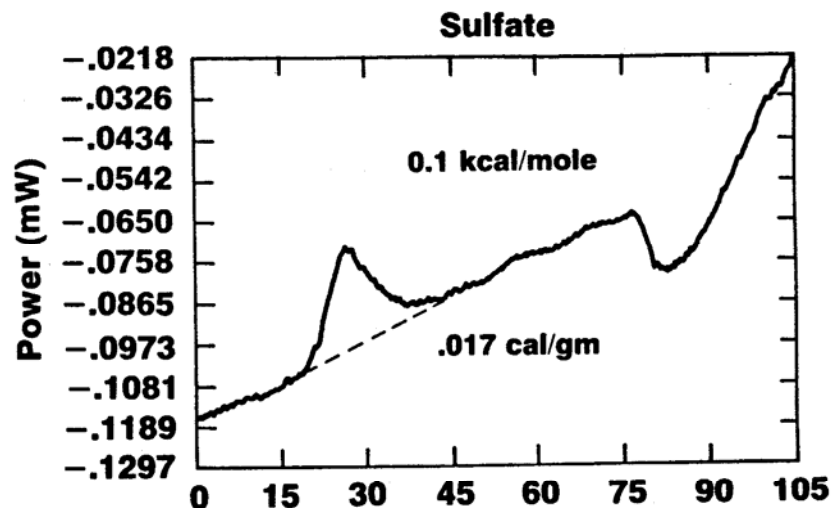
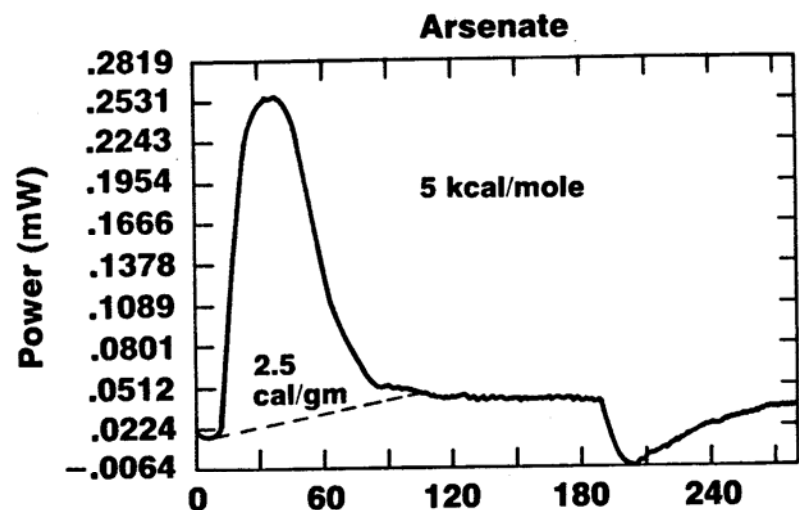
# Adsorption Thermodynamics

$$\Delta G_{\text{ads}} = \Delta G_{\text{coul}} + \Delta G_{\text{chem}} + \Delta G_{\text{soln}}$$

$\Delta G_{\text{coul}}$  = Free energy from coulombic interactions

$\Delta G_{\text{chem}}$  =  $\Delta G$  from specific chemical reactions,  
e.g., covalent surface bonds

$\Delta G_{\text{soln}}$  =  $\Delta G$  from changes in hydration of the  
sorbent, sorbate, and any other counter  
ions.



Heats evolved from adsorption of anions onto CPN  
Activated Alumina. pH 6.0,  $C_i = 100$  mg/L,  $T = 25.5^\circ\text{C}$   
J. W. Novak, Jr. and R. R. Burr, "Investigations of ion adsorption interactions using flow  
calorimetry", Alcoa Report 6-887-31

# Competing Ligands Sequence Activated Alumina (and FeOOH)

---



# Summary

- Adsorption of arsenic is its removal from water by concentration onto a porous adsorbent such as  $\text{AlOOH}$  or  $\text{FeOOH}$ .
- Adsorption of arsenic onto  $\text{AlOOH}$  and  $\text{FeOOH}$  is usually described using standard isotherms based on simple models, but it's a very complicated process.
- Surface complexes and ion pairs are formed, pH increase lowers arsenic adsorption. Competing anions such as silicate, phosphate, fluoride, vanadate, and sulfate also reduce arsenic adsorption.



That completes my  
presentation. Thank you for  
your attention.

Now, if there is time, I will  
answer questions.